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METHYLENE SINGLET-TRIPLET ENERGY SPLITTING BY MOLECULAR BEAM PH--ETC(U)  
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METHYLENE SINGLET-TRIPLET ENERGY SPLITTING  
BY MOLECULAR BEAM PHOTODISSOCIATION OF KETENE

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OCTOBER 1981

ABSTRACT

The singlet-triplet splitting in methylene has been determined from the measurements of fragment velocities from ketene photodissociation at 351 and 308 nm in a molecular beam. The splitting is found to be  $8.5 \pm 0.8$  kcal/mole. This agrees with many experimental results, but not with the value of 19.5 kcal/mole derived from recent photodetachment experiments on  $\text{CH}_2^+$ .

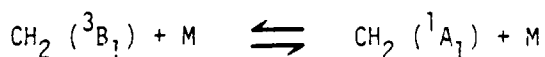
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## INTRODUCTION

The unique chemistry of the methylene radical,  $\text{CH}_2$ , is primarily due to the substantially different chemical behavior of two low lying electronic states, the ground ( $^3\text{B}_1$ ) state and the lowest excited ( $^1\text{A}_1$ ) state. The photochemical processes commonly used to produce  $\text{CH}_2$  can yield both states, and the nature of subsequent reactions depends on whether triplet or singlet methylene is involved. In spite of a large number of experimental and theoretical studies, questions about the energies of these states still remain.

Several different experimental approaches have been used to obtain information on these energies. Most of the results are consistent with a singlet-triplet splitting of about  $8.5 \pm 1$  kcal/mole, but the most direct measurement, the photoelectron spectrum of photodetachment from  $\text{CH}_2^-$ , gives 19.5 kcal/mole.<sup>1</sup> In addition, the best calculations show the energy difference to be around 10.5 kcal/mole, supporting the lower experimental value. The molecular beam photofragmentation translational spectroscopy on ketene described in this paper provides another microscopic experiment which eliminates many of the problems associated with other methods, and thus should help resolve the differences between the experimental results.

Measurements of the temperature and pressure dependence of product ratios from  $\text{CH}_2$  ( $^1\text{A}_1$ ) and  $\text{CH}_2$  ( $^3\text{B}_1$ ) reactions have been used to estimate the singlet-triplet energy difference assuming that collision induced transitions



maintain equilibrium concentrations of the two species. Values of  $7.5 \pm 0.7$  kcal/mole<sup>2</sup> and  $8.7 \pm 0.8$  kcal/mole<sup>3</sup> were then obtained. To determine the heat of formation of CH<sub>2</sub> (<sup>3</sup>B<sub>1</sub>), the threshold for production of CH<sub>2</sub><sup>+</sup> from dissociative photoionization has been measured using several different precursors. From known enthalpies of formation for the dissociating molecules, and the ionization potential of CH<sub>2</sub>, an upper limit has been placed on  $\Delta H_{fo}^0$  CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>). This will be the correct value if no excess energy is released in the dissociative photoionization at threshold. The enthalpy of formation of methylene (<sup>3</sup>B<sub>1</sub>) from this procedure ranges from 91.9 to 95.5 kcal/mole with the best values being  $93.8 \pm 0.4$  and  $93.4 \pm 0.4$  kcal/mole from photoionization of methane and ketene respectively<sup>4</sup> and  $94.6 \pm 0.5$  kcal/mole from methane.<sup>5</sup> The spread in these numbers can be accounted for by the difficulty in determining the thresholds, and in estimating the contributions of internal energy to the process. Recent work has also placed an upper limit on  $\Delta H_{fo}^0$  CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>). The internal excitation of methylene (<sup>1</sup>A<sub>1</sub>) produced from photodissociation of ketene with a nitrogen laser was determined by laser induced fluorescence. The temperature dependence of the fluorescence intensity from CH<sub>2</sub> was measured to estimate the amount of internal excitation that must be present in ketene for dissociation to occur at the nitrogen laser wavelength (337.1 nm). Then from the heats of formation of CH<sub>2</sub>CO and CO,  $\Delta H_{fo}^0$  CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) has been calculated, with the result.<sup>6</sup>

$$\Delta H_{fo}^0 \text{ CH}_2(^1\text{A}_1) = 101.7 \pm 0.5 \text{ kcal/mole.}$$

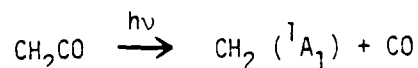
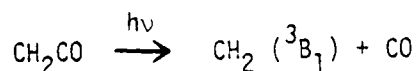
This upper limit should be close to the correct value if the internal energy in the CO fragment and the kinetic energy release are negligible.

In similar experiments the threshold for  $\text{CH}_2 (^1\text{A}_1)$  production from ketene was measured by monitoring methylene laser induced fluorescence as a function of photolysis laser wavelength. Independent determinations of the threshold gave  $85.0 \pm 0.3 \text{ kcal/mole}^6$  and  $85.4 \pm 0.3 \text{ kcal/mole}^7$  corresponding to

$$\Delta H_{\text{fo}}^0 \text{ CH}_2 (^1\text{A}_1) = 101.5 \pm 0.5 \text{ kcal/mole and} \\ 101.9 \pm 0.5 \text{ kcal/mole}$$

respectively.

The wavelength threshold for ketene photolysis at 298°K yielding  $\text{CH}_2 (^3\text{B}_1)$  and CO has also been determined from the appearance of CO product.<sup>8</sup> In the same experiment the threshold for ketene photolysis to give  $\text{CH}_2 (^1\text{A}_1)$  was measured by detecting products of the singlet-reacting with cis-2-butene. Thus enthalpies for the reactions



were determined at 298°K. The difference in the threshold energies then gave a value of  $8.3 \pm 1 \text{ kcal/mole}$  for the singlet-triplet energy splitting.

The studies mentioned above and many other similar experiments are all consistent with a  $\text{CH}_2$  ( $^3\text{B}_1$ ) -  $\text{CH}_2$  ( $^1\text{A}_1$ ) splitting of  $8.5 \pm 1$  kcal/mole, but the most direct observation of the splitting, the photoelectron spectrum from the photodetachment of  $\text{CH}_2^-$  to produce  $\text{CH}_2$  ( $^1\text{A}_1$ ) and  $\text{CH}_2$  ( $^3\text{B}_1$ ) has been interpreted to show a splitting of 19.5 or 23.2 kcal/mole.<sup>1</sup> There are several possible explanations for this apparent contradiction. If the singlet-triplet splitting is indeed about 8.5 kcal/mole, then the photoelectron spectrum is not correctly assigned, and perhaps hot bands of  $\text{CH}_2^-$  are being observed.<sup>9,10</sup> Franck-Condon factors for the photodetachment of an electron from  $\text{CH}_2^-$ , have been calculated from ab initio potential curves, and fit the observed spectra well if it is assumed that hot bands are present.<sup>9</sup> This assignment predicts a  $^1\text{A}_1$  -  $^3\text{B}_1$  splitting of  $9 \pm 1$  kcal/mole, but extensive experimental work attempting to confirm the presence of hot bands has tended to show that the observed features are not due to vibrationally excited  $\text{CH}_2^-$ .<sup>1</sup> If the methylene singlet-triplet splitting is actually around 20 kcal/mole, then it is difficult to explain the photochemical and photoionization results. An upper bound for  $\Delta H_{\text{fo}}^0 \text{CH}_2$  ( $^1\text{A}_1$ ) is firmly established, within the accuracy of the corrections for the effects of reactant internal excitation to photodissociation ( $\pm 1$  kcal/mole). Thus for the splitting to be as large as 20 kcal/mole the apparent thresholds in the photolysis and dissociative photoionization experiments used to determine  $\Delta H_{\text{f}} \text{CH}_2$  ( $^3\text{B}_1$ ) must be 11.5 kcal/mole higher than the actual thermodynamic limit and this

amount of excess energy must be released at the threshold. The reduction of the heat of formation of  $\text{CH}_2$  ( $^3\text{B}_1$ ) by as much as 10 kcal/mole is also not compatible with the results of many chemical activation studies of unimolecular decomposition.<sup>11</sup>

Many theoretical studies of methylene energy levels have been performed, and the most extensive ab initio calculations have given the values  $10.4 \pm 2$ ,<sup>12</sup> 10.5,<sup>13,14</sup> 10.6,<sup>15</sup> and 11.0 kcal/mole<sup>10</sup> for the singlet-triplet splitting. There is still a question of the exact correction to these calculations necessary to account for the differences in zero point energy of the two states. Harding and Goddard<sup>9</sup> calculated total zero point energies using the harmonic approximation and found a very small (0.16 kcal/mole) difference between the singlet and triplet. The result (10.4 kcal/mole) was corrected for this effect. Thus the theoretical results tend to support the lower (~8.5 kcal/mole) experimental value for the splitting but do not accurately agree with it.

By detecting the products of the photofragmentation of ketene in a molecular beam experiment, many of the uncertainties in other measurements of the methylene singlet-triplet splitting can be avoided. In particular the velocity of the fragments can be directly measured and the translational energy distribution determined. The maximum translational energy released in the dissociation should correspond to the production of ground state  $\text{CH}_2$  and CO, and even if there



is a barrier for dissociation, the potential energy will be transformed into product translational and internal energy. A further advantage is that the expansion which produces the molecular beam cools the ketene sufficiently that its internal energy can be neglected.

## EXPERIMENTAL

The experiments were performed in a crossed molecular beams machine, with a laser replacing one of the molecular beam sources. The laser and molecular beams cross at  $90^\circ$  in an interaction chamber, where the pressure is maintained at about  $1 \times 10^{-7}$  torr. The detector is a quadrupole mass spectrometer which can be rotated around the crossing point in the plane determined by the two beams. Photo-fragments which pass through the detector entrance slit and two stages of differential pumping enter the ionization chamber where they are ionized by electron impact. The slits used were chosen to give a laboratory angular resolution of  $2.5^\circ$ . The ions pass through the quadrupole mass selector to a Daly detector. The neutral products travel a distance of 34.1 cm to the ionizer after dissociation. The time interval between the laser pulse and the detection of the products is recorded in a multichannel scaler, allowing the fragment's recoil velocity to be determined.

Ketene was prepared by pyrolysis of acetic anhydride and trapped at  $77^\circ\text{K}$ . A portion was purified for use each day by trap to trap distillation. A supersonic beam of ketene seeded in helium was produced by bubbling helium through liquid ketene in a dry ice-ethanol bath, and expanding the resulting mixture at 300 torr through a 0.22 mm nozzle. After passing through two stages of differential pumping and collimation, the beam, with a spread of  $2.5^\circ$ , entered the interaction chamber.

The beam of ketene had a peak velocity of  $1.12 \times 10^5$  cm/sec and a full width at half maximum velocity spread of about 10%. The density of ketene in the interaction region was about  $10^{11}$  molecules/cc.

A Lumonics Model TE-861 rare gas halide excimer laser was used at 351 nm (XeF) and 308 nm (XeCl) for the photodissociation. The laser beam was focused to a spot of about 0.5 cm diameter where it crossed the molecular beam and was operated at 70 Hz with a measured average power of about 2.5 watts at both wavelengths.

## RESULTS AND ANALYSIS

The data obtained in this experiment consist of time-of-flight distributions which are proportional to the number density of the detected product present in the mass spectrometer ionizer as a function of time after the laser pulse. To determine the thermochemical quantities of interest the data must be converted to energy distributions in the center of mass coordinate system of the dissociating molecule. Figure 1 shows a velocity vector diagram for the process. The origin of the lab coordinate system is the base of the beam velocity vector and lab angles are measured from the direction of the beam. The tip of this vector defines the origin of the center of mass coordinate system and the circles show CO fragment velocities corresponding to various product translational energies.

It was found necessary to make a small background correction to the raw data, as a result of the large detector apertures used to enhance the signal to noise ratio in this experiment. These large apertures allow some product molecules to strike surfaces of the ionizer and raise the background for a short time after each laser pulse. The background then decays exponentially with a time constant determined by the pumping speed for that molecule. Correction for this minor effect was made by requiring the background for times where signal cannot appear due to kinematic constraints to be equal to the background before the first signal arrived. The behavior of the time dependent background was simulated with an amplitude proportional to the intensity of signal, and a decay constant

roughly corresponding to the pumping speed, and then subtracted from the data. These two parameters could be varied until the proper background level was obtained. An example of original and corrected data is shown in Fig. 2. All further CO data shown in Figs. 3 and 5 has been corrected in this manner. The problem does not appear for CH<sub>2</sub>, apparently because it is rapidly destroyed by wall collisions.

The determination of the center of mass energy distribution is done by an iterative process. A trial energy and angular distribution is used as the input to a computer simulation program. The energy distribution is converted to center of mass velocity flux according to the relation:

$$I_{c.m.}(u, \vartheta_{cm}) \propto u I_{cm}(E_{cm}, \vartheta_{cm})$$

This is then transformed to laboratory time-of-flight.

$$N_{LAB}(t, \vartheta_{LAB}) \propto \frac{v^3}{lu^2} I_{cm}(u, \vartheta_{cm})$$

where  $l$  is the flight path, and  $v$  and  $u$  are lab and c.m. velocity respectively. The beam velocity and angular spreads are accounted for by summing the contributions due to different initial speeds and angles. The detector resolution is included in a similar fashion. The result for a given center of mass energy distribution was compared to the data, and the input changed until the agreement was satisfactory.

The center of mass distributions used had the form

$$I_{cm}(E_{cm}, \theta_{cm}) = P(E_{cm}) D(\theta_{cm})$$

The energy distribution itself was

$$P(E) = C(E - E_1)^\alpha (E_T - E)^\beta$$

For convenience in fitting the data the actual parameters used in the computer simulation were  $E_p$ , the energy at which the distribution peaks;  $E_p - E_1$ , the difference between the peak and the low energy at which the probability goes to zero; and  $E_T - E_p$ , the difference between the high energy where the probability goes to zero and the peak. The parameter  $\alpha$  can then be calculated for given  $\beta$ ,  $E_p$ ,  $E_1$  and  $E_T$

$$\alpha = \frac{3(E_p - E_1)}{E_T - E_p}$$

Several distributions could be added together to produce the best fit to the data.

An energy and angular distribution was chosen for each laser frequency which most closely fit all the data taken at different angles. The results for the XeF laser at 351 nm are shown in Fig. 3. The fit (solid line) is superimposed on the data (solid dots). An angular distribution of  $1 + \sin^2\theta$  produced the best agreement with the data. The time-of-flight for CO products could be fit with the same energy distribution at the two angles, but for the CH<sub>2</sub> product the entire distribution had to be shifted 0.5 kcal/mole to higher energy. For

determining the thermodynamic quantities discussed later, the center of mass energies consistent with the data from the CO fragment were used since the signal to noise is much better than for the CH<sub>2</sub> fragment. The energy distribution is shown in Fig. 4, and the actual values used for the parameters are shown in Table 1. Figure 3 also shows the result of calculations of the laboratory time of flight at 14° if the center of mass energies are shifted up and down by 1 kcal/mole without changing the shape of energy distribution. This gives an idea of the sensitivity of the experiment. The results for the CO fragment when ketene is dissociated with the 308 nm light from the XeCl laser are shown in Fig. 5. All angles are fit with the same energy distribution as shown in Table 1, and an angular distribution  $1 + \cos^2\theta$  was used. The energy distribution is shown in Fig. 6. Again the sensitivity to energy shifts of 1 kcal/mole are shown (Fig. 5) for a lab angle of 14°. Because of the larger product translational energy released at this frequency the sensitivity to the threshold energy distribution is less than that at 351 nm.

From the energy distributions determined in this experiment several thermochemical quantities related to ketene dissociation can be derived. The expansion producing the supersonic beam using He carrier gas cools the ketene sufficiently that it can be assumed the molecule starts essentially in its ground state. A photon of known energy is absorbed, and we then measure the translational energy of the fragments. Because the sum of the translational energy and internal energy is the excess energy available for dissociation, the fastest products detected should correspond to ground state CO and CH<sub>2</sub> formation. Several previous experiments<sup>6,7,16</sup>

have shown that the threshold for  $\text{CH}_2$  ( $^1\text{A}_1$ ) production from ground state ketene is substantially above the energy supplied by a 351 nm photon, so the signal at this wavelength must be due entirely to  $\text{CH}_2$  ( $^3\text{B}_1$ ). From the distribution in Fig. 4 the highest translational energy observed in the products is 3.8 kcal/mole. When this is subtracted from the 81.4 kcal/mole supplied by the photon it gives a value of 77.6 kcal/mole for the bond dissociation energy of  $\text{CH}_2\text{CO}$  to  $\text{CH}_2$  ( $^3\text{B}_1$ ) and CO. Photons at 308 nm from the XeCl laser energetically could produce both singlet and triplet methylene, but we observed only singlet. If triplet products were produced they would be considerably faster than the fastest signal observed. Figure 7 shows a simulated time-of-flight spectrum from an energy distribution which is the same as that used to fit the data at 308 nm, except for the addition of a second distribution at an energy corresponding to that expected for the triplet, as determined from the result at longer wavelength. The second distribution has a peak 10% as high as the peak of the singlet distribution. The actual data shows no similar features in the corresponding position. Thus the highest translational energy products are assumed to be ground vibrational and rotational state  $\text{CH}_2$  ( $^1\text{A}_1$ ) and CO. Subtracting the translational energy (6.7 kcal/mole) of these products from the laser photon energy of 92.8 kcal/mole results in 86.1 kcal/mole for the bond dissociation of ketene to produce  $\text{CH}_2$  ( $^1\text{A}_1$ ) and CO. Thus the energy difference between the singlet ( $^1\text{A}_1$ ) and triplet ( $^3\text{B}_1$ ) states of  $\text{CH}_2$  is 8.5 kcal/mole,



with an uncertainty of approximately 0.8 kcal/mole, mainly from the experimental determination of the maximum translational energy release. These results are summarized in Fig. 8.

From the known heats of formation of  $\text{CH}_2\text{CO}$  ( $\Delta H_{\text{fo}}^{\circ} = -10.7$  kcal/mole)<sup>17</sup> and  $\text{CO}$  ( $\Delta H_{\text{fo}}^{\circ} = -27.199$  kcal/mole),<sup>18</sup> the heat of formation of  $\text{CH}_2$  can be calculated from the measured bond dissociation energies of  $\text{CH}_2\text{CO}$ .

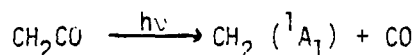
$$\begin{aligned}\Delta H_{\text{fo}}^{\circ} (\text{CH}_2 \ ^3\text{B}_1) &= 77.6 \text{ kcal/mole} + \Delta H_{\text{fo}}^{\circ} (\text{CH}_2\text{CO}) \\ &- \Delta H_{\text{fo}}^{\circ} (\text{CO}) = 94.1 \text{ kcal/mole}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{fo}}^{\circ} (\text{CH}_2 \ ^1\text{A}_1) &= 86.1 \text{ kcal/mole} + \Delta H_{\text{fo}}^{\circ} (\text{CH}_2\text{CO}) \\ &- \Delta H_{\text{fo}}^{\circ} (\text{CO}) = 102.6 \text{ kcal/mole}\end{aligned}$$

## DISCUSSION

The value for the singlet-triplet splitting obtained from this work (8.5 kcal/mole) agrees very well with the lower value from previous experiments. The actual heats of formation derived from our results also compared favorably with those previously determined. The very close agreement of the photoionization value for  $\Delta H_{fo}^0$   $\text{CH}_2$  ( $^3\text{B}_1$ )<sup>4,5</sup> with the number from our experiments, where translational energy release is observed directly, strongly supports the assumption that there is no excess energy release at the threshold of ionization. It also tends to confirm that the fastest products we observed from dissociation with 351 nm photons do correspond to ground vibrational state CO and  $\text{CH}_2$ .

The threshold for the process



measured in several experiments are in fairly close agreement. In the work of Lengel and Zare the value  $85.2 \pm 0.3$  kcal/mole was obtained.<sup>6</sup> The similar experiments of reference 7 yielded  $85.4 \pm 0.3$ . Simons and Curry found  $84.4 \pm 0.6$  kcal/mole, for the process at 298°K.<sup>8</sup> All of these determinations rely on the translational energy release being negligible at the threshold. Again the assumption seems to be valid as our value of  $86.1 \pm 0.5$  kcal/mole agrees fairly well if the uncertainty in corrections of previous results for reactant internal energy is considered.

A large discrepancy exists between the results of this work, and the photodetachment results from  $\text{CH}_2^-$ , which support a large singlet-triplet splitting (19.5 kcal/mole).<sup>1</sup> As previously discussed, an upper limit can be placed on the energy of the  $\text{CH}_2$  ( $^1\text{A}_1$ ) state from previous experiments as well as from this work, so possible errors resulting in too small a value for the splitting must arise from placing the energy of the ( $^3\text{B}_1$ ) state too high. If the photodissociation of ketene at 351 nm produces no ground vibrational state products then the value of  $\Delta H_{\text{fo}}^0 \text{CH}_2$  ( $^3\text{B}_1$ ) determined in this experiment would be too high. This is very unlikely for several reasons. The heat of formation of triplet methylene we obtained agrees closely with previous measurements by completely different methods. It's difficult to imagine that identical errors appear in each case. In addition, if the splitting were as large as 19.5 kcal, then 15 kcal/mole is available to the products in the ketene dissociation at 351 nm. A maximum of 3.8 kcal appears as translation in our experiments. If there were at least another 11.0 kcal/mole of energy in the internal excitation of products, the product vibrational states would be very highly inverted. This is not expected since the CO vibration and the  $\text{CH}_2$  bending vibration both are strongly coupled to the reaction coordinate of the photodissociation of ketene, and the CO bond length in  $\text{CH}_2\text{CO}$  is quite close to that of CO.

There are several other interesting features of the center of mass energy distributions determined in this experiment. The shapes of the distribution of product energy at the two wavelengths are

obviously very different. For the triplet (from 351 nm dissociation) the product is fairly sharply peaked near the maximum translational energy release. The second smaller peak in Fig. 4 is necessary to fit the small feature in the time of flight data at  $14^\circ$ . The spacing between the two peaks is approximately equal to the energy of the bending vibration in ground state  $\text{CH}_2$  (3.4 kcal/mole).<sup>1</sup> This suggests that a small fraction of the  $\text{CH}_2$  is produced vibrationally excited. The translational energy distribution for singlet  $\text{CH}_2$  production from 308 nm dissociation (Fig. 6) peaks at zero translational energy and is very broad. This shows that there is substantial internal excitation of the products. The drastic change in the dissociation dynamics between 351 nm and 308 nm and the exclusive production of  $\text{CH}_2$  ( $^1\text{A}_1$ ) at 308 nm might suggest that different electronic states of ketene are involved at these two frequencies. The difference between the angular dependence of the product intensity at the two wavelengths is further evidence that the dissociation process changes in this wavelength region, but due to the limited angular range covered in these measurements our data is not sufficient to provide precise information on the angular distribution.

There is still some disagreement between the results of ab initio calculations of the singlet-triplet splitting ( $\sim 10.5$ ) and the experimental determination ( $\sim 8.5$  kcal/mole), although considering the uncertainty of  $\pm 1$  kcal/mole in each of these values they are not incompatible. A very recent, large scale CI calculation involving 60,000 configurations<sup>13</sup> has not brought the numbers any closer to

agreement, but correction for the difference in zero point energies was found to reduce the energy difference by 0.6 kcal/mole.<sup>19</sup> A small relativistic correction, at most 0.1 kcal/mole,<sup>20,21</sup> could reduce the calculated value of the splitting to 9.8 kcal/mole. It has also been suggested,<sup>15</sup> based on comparison of extensive CI calculations with experimental measurements of excited state energies for carbon atoms and CH, that the value for the singlet-triplet splitting in CH<sub>2</sub> from CI calculations is still somewhat too high and the actual separation is less than 10 and perhaps as small as 9 kcal/mole.

## CONCLUSION

This paper has described the measurement of the energy splitting between the ground ( $^3B_1$ ) and first excited ( $^1A_1$ ) states of methylene. The experiment was especially designed to detect possible barriers to photodissociation which potentially could have caused errors in previous results. No evidence for such barriers was observed and our value of 8.5 kcal/mole agrees well with the majority of other experiments attempting to measure the singlet-triplet splitting.<sup>2,3,6,7,8,22</sup> It is also in reasonable agreement with recent ab initio quantum mechanical calculations,<sup>10,12,13,14,15</sup> but not with the larger value obtained from the photoelectron spectrum of photodetachment from  $CH_2^-$ .<sup>1</sup>

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Table 1. Center of mass energy distribution parameters for the photodissociation of  $\text{CH}_2\text{CO}$ . Energies are in kcal/mole.

	$E_p$	$E_T - E_p$	$E_p - E_1$	3	Peak Height
351 nm dissociation					
CO product at 14° and 17°					
(Fig. 3) High energy peak	2.3	1.5	1.2	2.5	1.0
(Fig. 4) Low energy peak	.45	.40	.40	1.3	.3
351 nm dissociation					
CH <sub>2</sub> product at 35° (Fig. 3)					
	2.8	1.5	1.2	2.5	1.0
308 nm dissociation					
CO product at 14°, 17°, 20° and 25° (Fig. 5 and Fig. 6)					
	0.0	6.7	0.0	1.2	1.0
308 nm dissociation					
CO product at 14°					
Singlet	0.0	6.7	0.0	1.2	1.0
Triplet	9.2	6.0	4.8	2.5	0.1
(Fig. 7)					

#### FIGURE CAPTIONS

Fig. 1. Newton diagram for photodissociation of  $\text{CH}_2\text{CO}$  showing relations between laboratory and center of mass velocities and angles.

$V_{\text{CH}_2\text{CO}}$  and  $V_{\text{CO}}$  are laboratory velocity vectors,  $U_{\text{CO}}$  is a center of mass velocity vector. The origin of the lab coordinate system is the base of the vector for the initial  $\text{CH}_2\text{CO}$  velocity, and the origin for the center of mass system is the tip of the same vector. The circles have radii corresponding to the speed of the CO fragment in the center of mass frame for various amounts of translational energy release in the dissociation.

Fig. 2. Time of flight data at a lab angle of  $14^\circ$  for the CO fragment from  $\text{CH}_2\text{CO}$  photodissociation at 308 nm. The dots are the original data, and the solid line shows the data after subtraction of time dependent background.  $N(t)$  is the number of counts as a function of time (arbitrary units).

Fig. 3a. Time of flight data for fragments from ketene photodissociation at 351 nm and various lab angles.  $N(t)$  is the number of counts per time channel (arbitrary units). Dots are the data, the solid lines are the fits.  $E_{\text{+}}$  is the highest center of mass energy (kcal/mole) with non-zero probability in the energy distributions used for the computer simulation. The energy distribution has been shifted  $\pm 1$  kcal/mole to show the sensitivity of the fits.

Fig. 3b. Time of flight data and computer generated fits for the CO fragment at  $17^\circ$  lab angle and the  $\text{CH}_2$  fragment at  $35^\circ$  lab angle from ketene photodissociation with the laser operated at 351 nm.

Fig. 4. Center of mass energy distribution for ketene photofragmentation at 351 nm. The energy scale is in kcal/mole. This distribution was used to fit the data for the CO fragment at lab angles of  $14^\circ$  and  $17^\circ$ . The actual parameters are given in Table I.

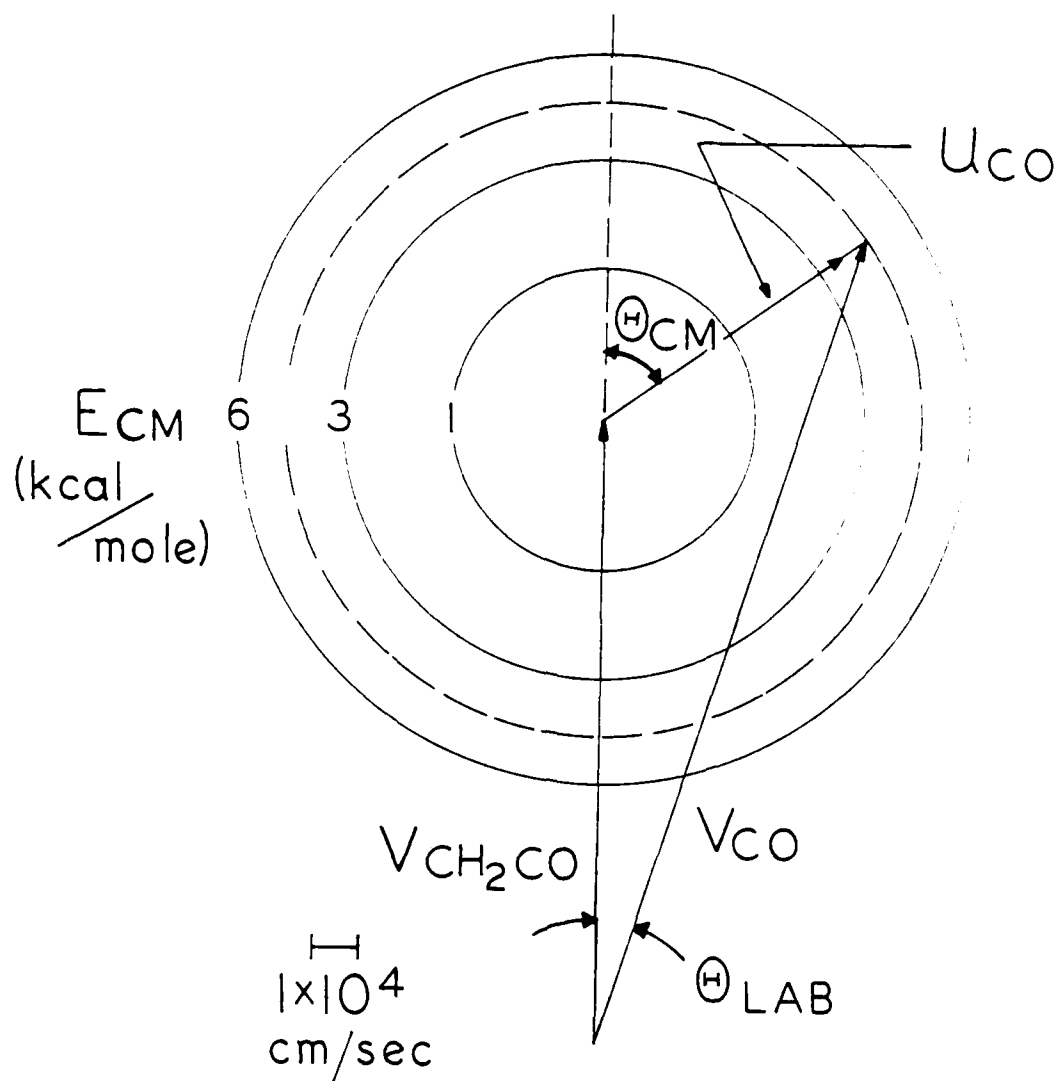
Fig. 5a. Time of flight data for the CO fragment from ketene photodissociation at 308 nm and  $14^\circ$  lab angle.  $N(t)$  is the number of counts per time channel (arbitrary units). Dots are the data, lines are the computer generated fits. The time of flight spectrum has been calculated for the center of mass energy distribution with parameters shown in Table I, and with  $E_T$  shifted  $91$  kcal/mole.

Fig. 5b. Time of flight data and computer generated fits for the CO fragment from photodissociation of ketene at 308 nm and various lab angles.

Fig. 6. Center of mass energy distribution for ketene photodissociation at 308 nm. Energy scale is in kcal/mole. The distribution shown was used to fit all the CO time of flight data from the 308 nm dissociation. The parameters for this distribution are given in Table. I.

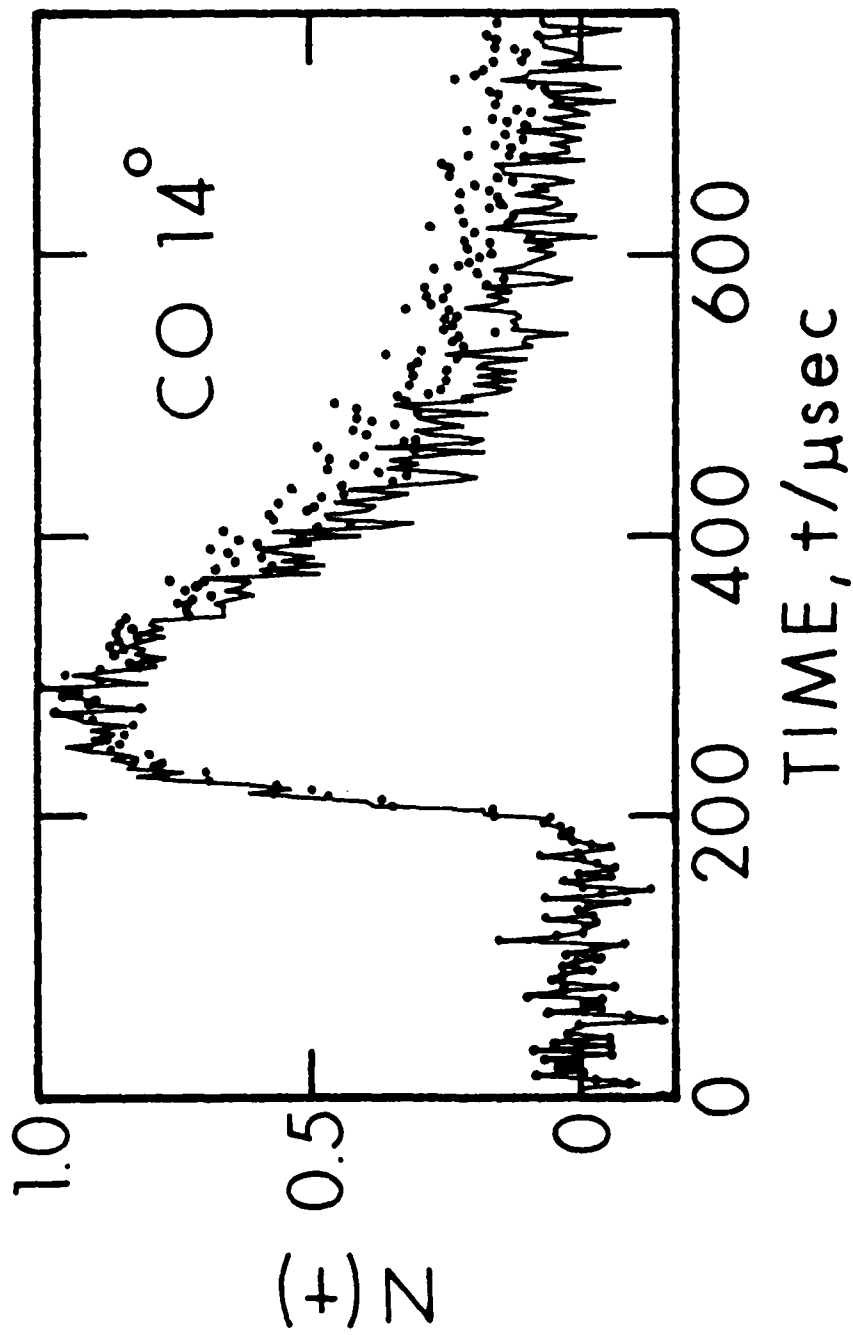
Fig. 7. The dots show the time of flight data for the CO fragment at  $14^\circ$  from  $\text{CH}_2\text{CO}$  photodissociation with 308 nm light. The solid line is the computer calculated time of flight spectrum for CO fragments if a center of mass energy distribution corresponding to  $\text{CH}_2$  ( $^3\text{B}_1$ ) production at this wavelength is added to the distribution actually used to fit the data. The parameters used to generate this figure are shown in Table I.

Fig. 8. Energy level diagram for the ketene photodissociation process. All energies shown are in kcal/mole.



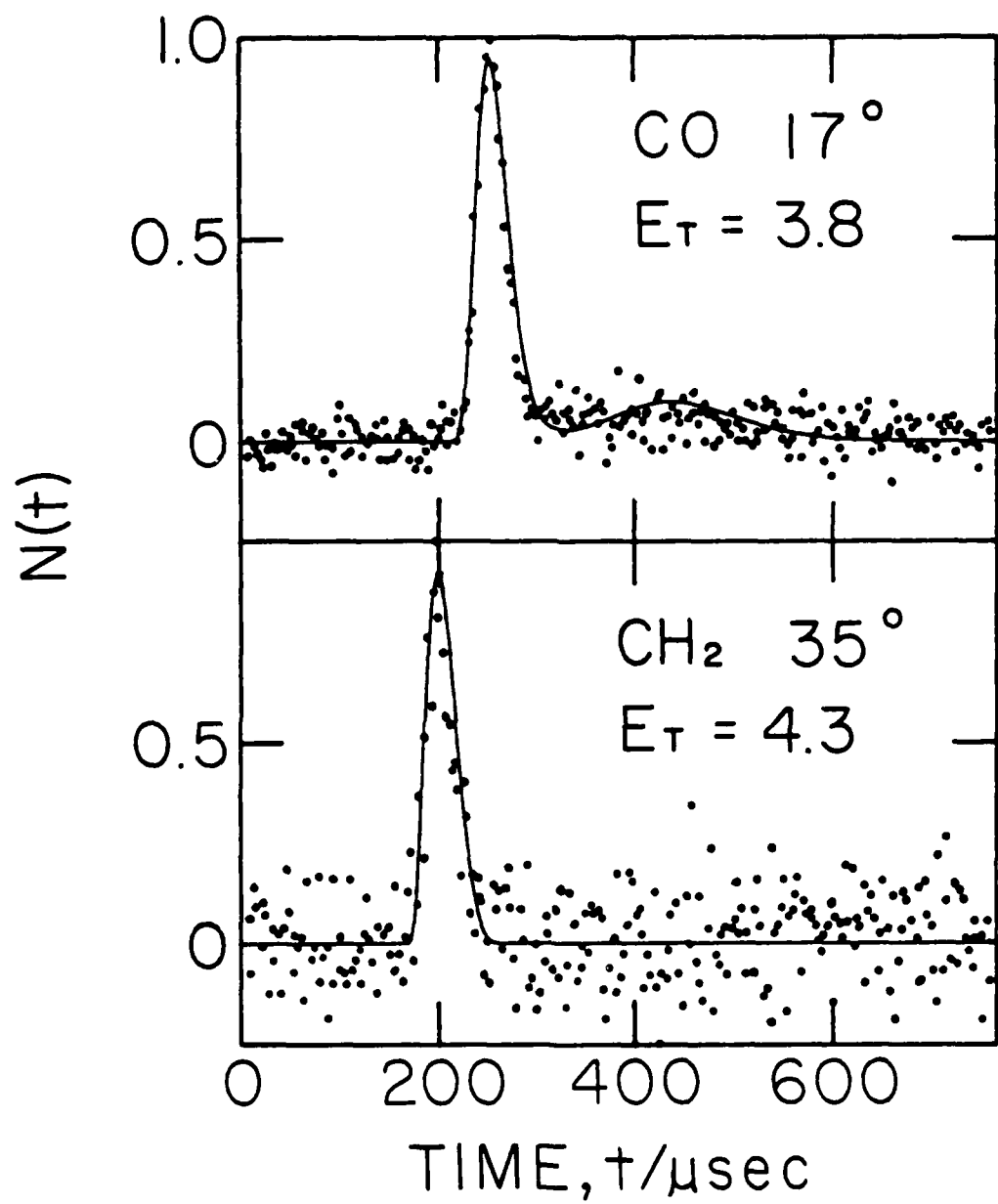
XBL 811-7778

Fig. 1



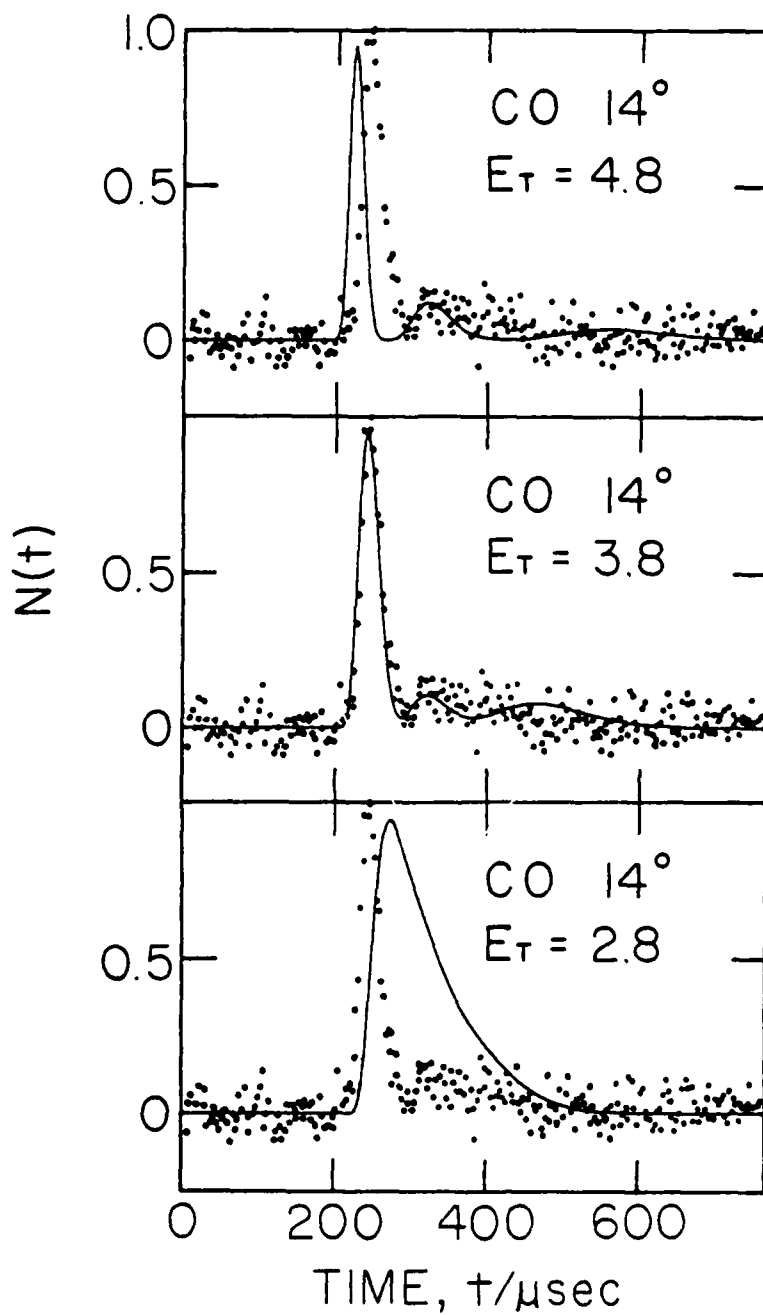
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Fig. 2



XBL 819-1796

Fig. 3a.



XBL 319-1797

fig. 2b.



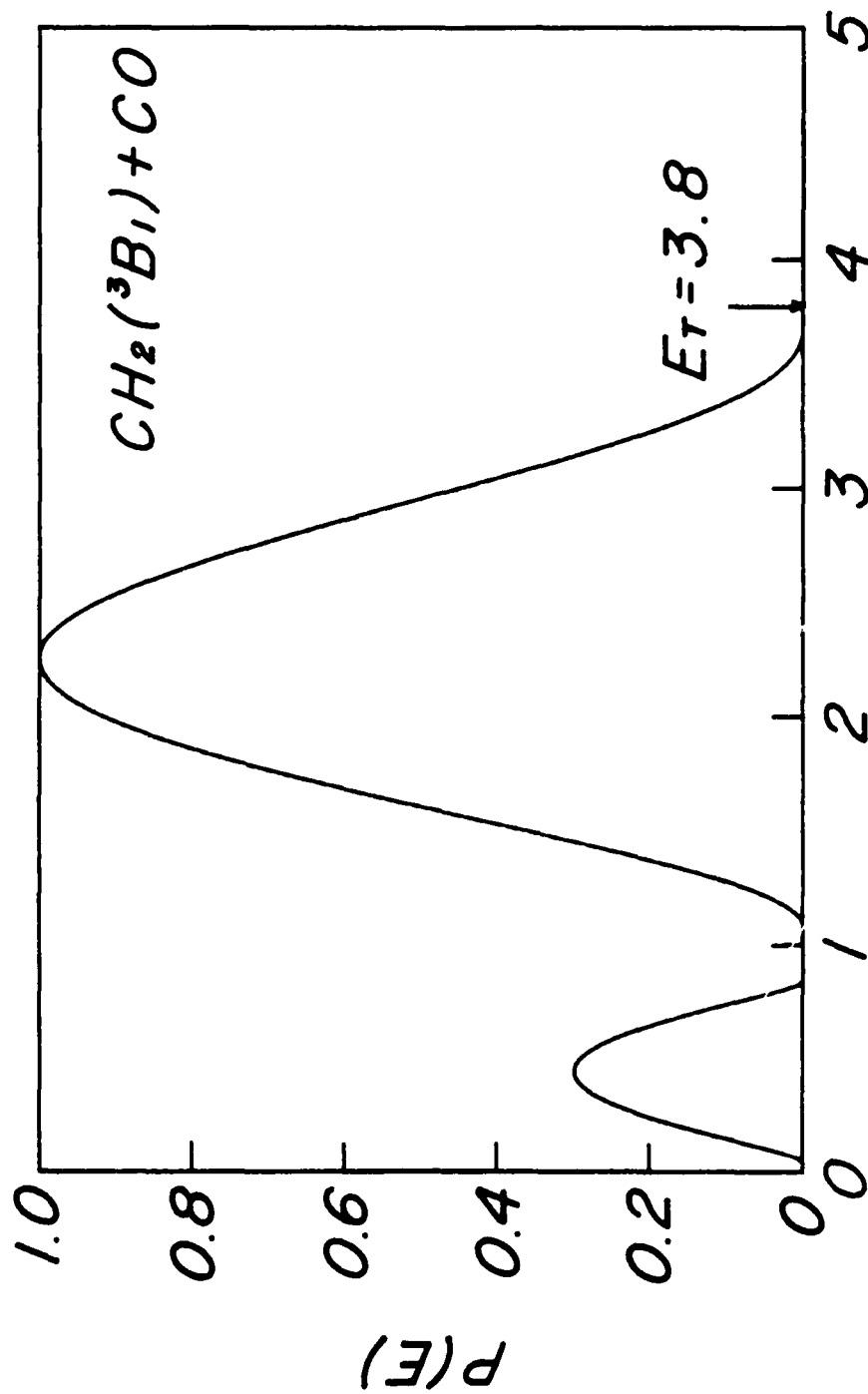
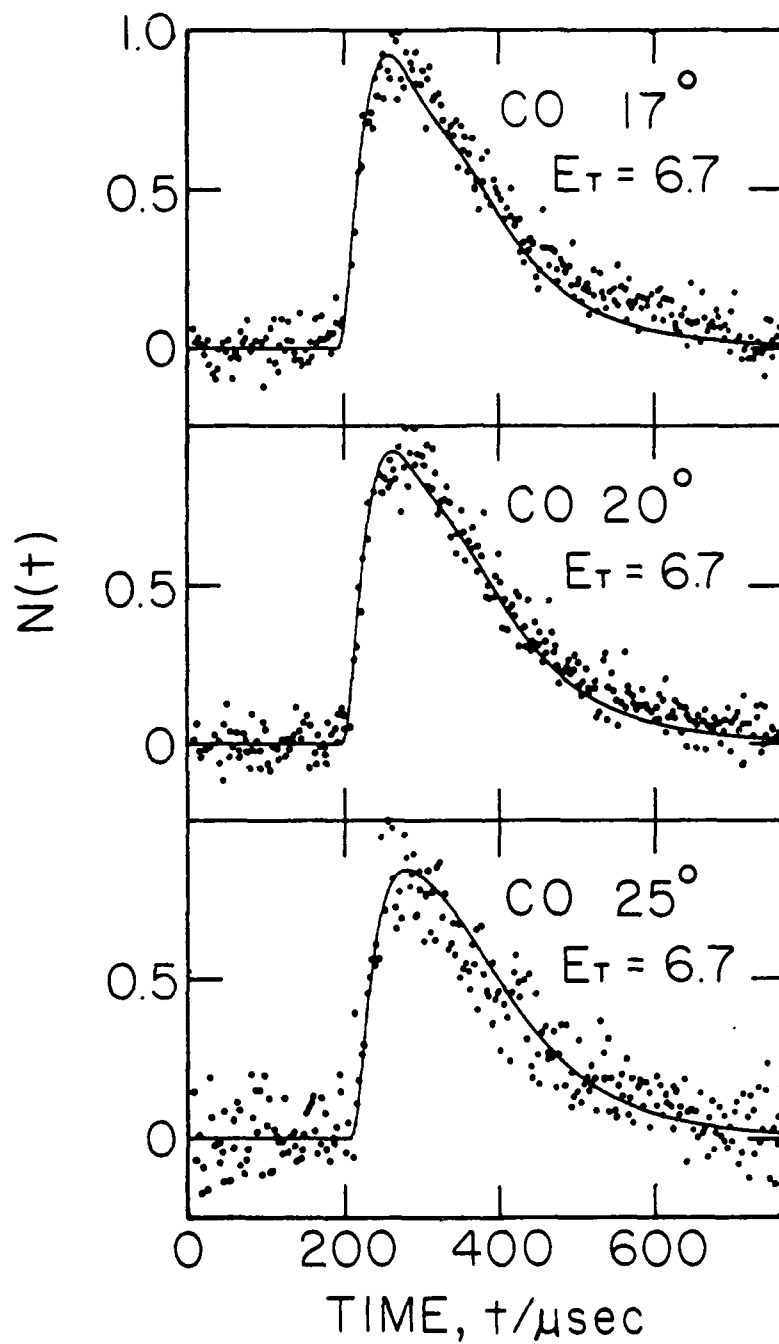


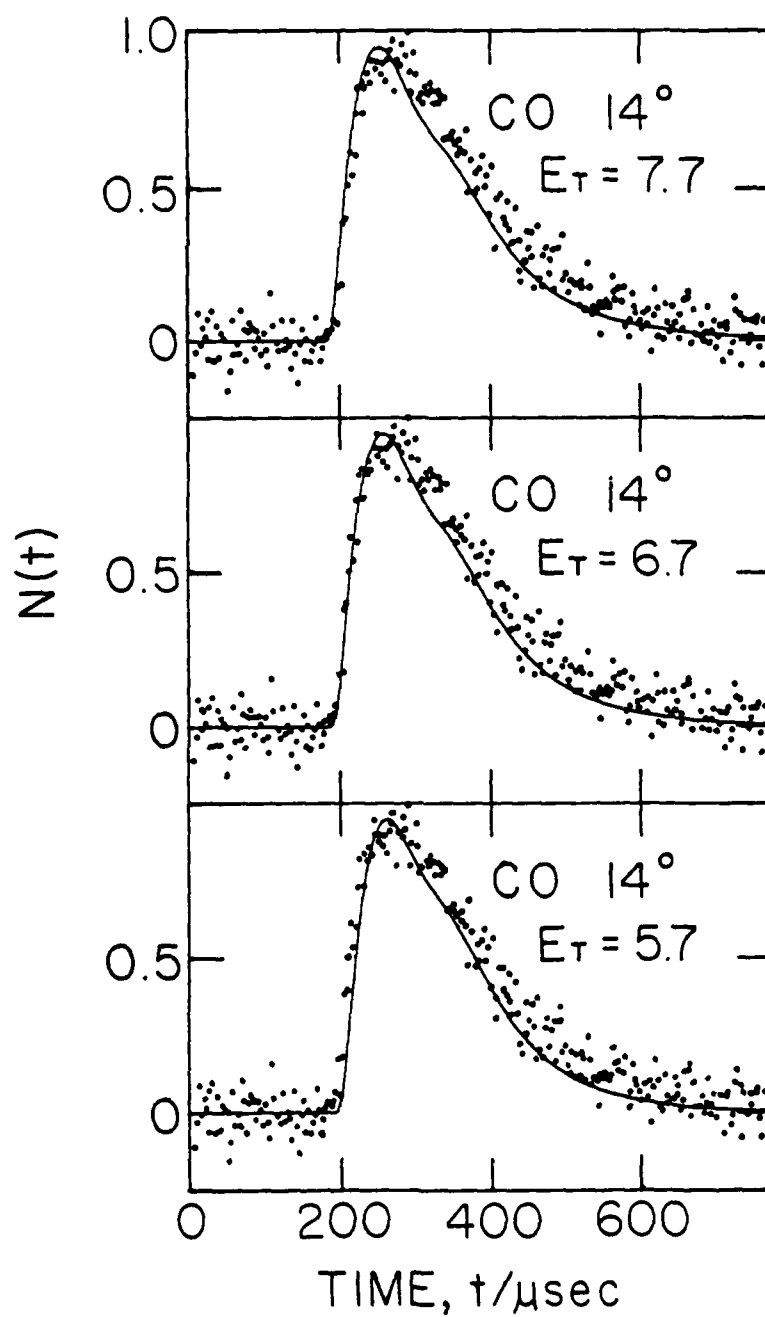
Fig. 4

XBL 811-7782



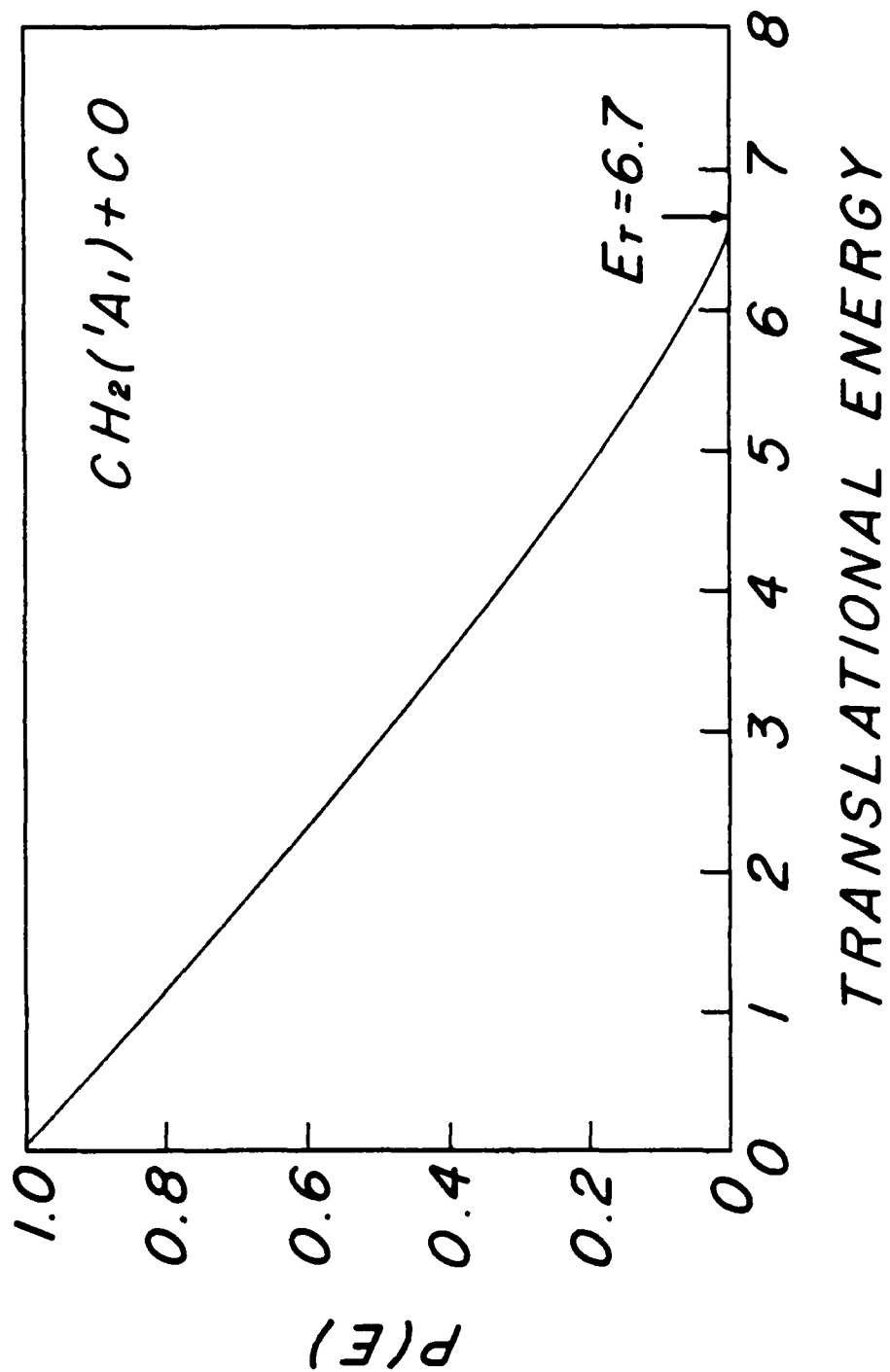
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Fig. 5a.



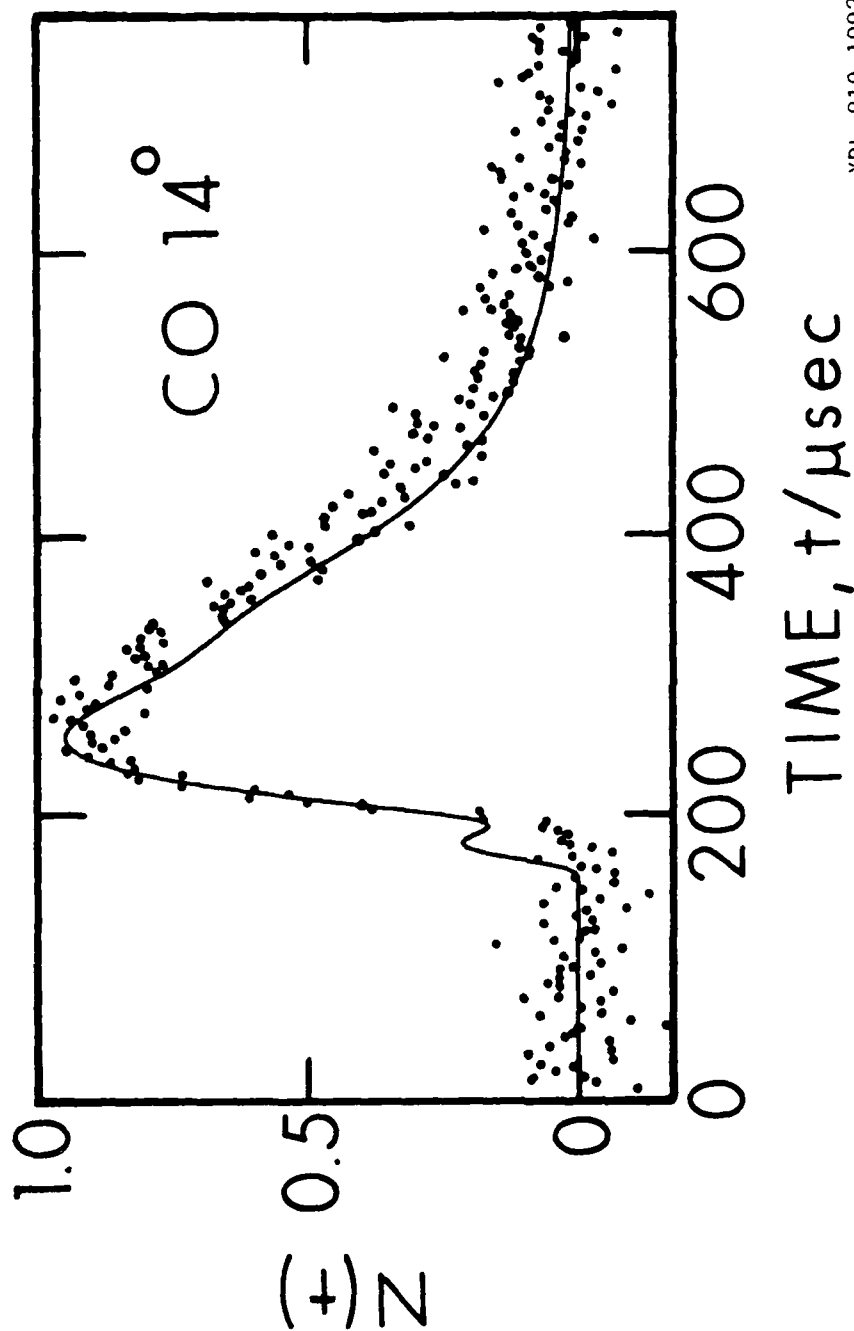
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Fig. 30.



14. 6.

XBL 811-7783



XBL 819-1992

Fig. 7.

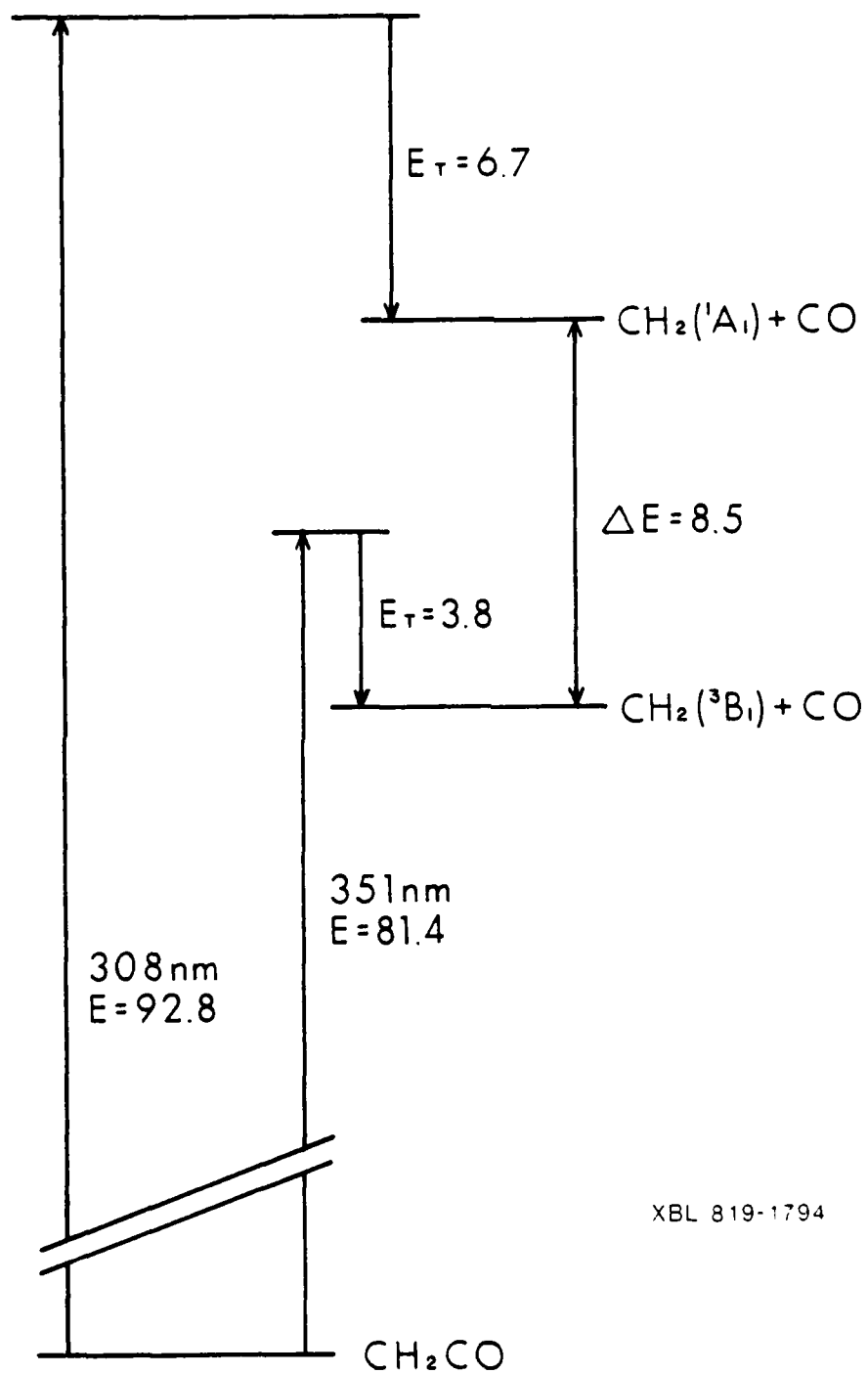


Fig. 3.

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